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Schlumberger Holdings Limited

PO Box 71
Craigmuir Chambers
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Patents ADP number (if you know it)

British Virgin Islands

7236326001

4. Title of the invention

APPARATUS AND METHOD FOR MEASURING CONCENTRATIONS OF IONS IN DOWNHOLE WATER

5. Name of your agent (if you have one)

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

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01223 325268

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DUPLICATE

APPARATUS AND METHOD FOR MEASURING CONCENTRATIONS OF IONS
IN DOWNHOLE WATER

5 Field of Invention

This invention relates to the determination of ion concentrations in downhole water from hydrocarbon wells, aquifers etc. This is useful in a wide range of applications, including predicting the formation of scale and fingerprinting waters from different sources.

10

Background

The prediction of the location and type of mineral scale that may form around or within the production or surface facilities of an oil well is an important factor both in 15 the design of the well and the formulation of strategies to cope with the mineral scale.

Current methods for predicting mineral scale formation involve the retrieval of samples from downhole, which are 20 then either analysed at the surface or else sent off to laboratories for analysis. Errors and delays can arise from this *ex situ* analysis.

Electrochemical methods have previously been developed 25 for the measurement of the concentration of a number of different metal ions, and some have been deployed in shallow boreholes, lakes and ocean waters. However, the application of these methods to oilfield operations has been limited, as the high temperatures (up to 175 30 Celsius) and pressures (up to 1500 bar) common to most reservoirs, make their use impractical. Furthermore, many electrochemical methods are not able to distinguish

between the principal metal ions (Ca^{2+} , Ba^{2+} and Sr^{2+}) responsible for scale formation. This problem is compounded by the low concentrations of these ions (about 10s mg/L) in formation water which is often highly saline.

5 The ability to rapidly and conveniently distinguish scaling ions may also find application, for example, in fingerprinting waters flowing into a hydrocarbon well 10 from different producing zones. This information, which is indicative of connectivity between different zones of a producing well, may allow the optimization of production strategies for recovering the oil in place.

Summary of the Invention

15 An object of the invention is to provide improved methods for the measurement of the scaling ions, which are suitable for use *in situ* i.e. under downhole conditions.

20 Accordingly, a first aspect of the invention provides an apparatus for determining the concentration of scaling ions in downhole water; the apparatus comprising;

25 a ligand which binds scaling ions in a sample of downhole water, said ligand having an electronic configuration which is altered on binding of a scaling ion, and;

30 a detector for determining alterations in said electronic configuration, the amount of said alterations being indicative of the concentration of the scaling ion in the sample.

35 Preferably the ligand is contained within an electrochemical cell and changes in the electroactivity of the ligand are determined, for example

amperometrically or voltammetrically. In other embodiments, the binding of a scaling ion may alter the fluorescent properties of the ligand. Changes in the fluorescence of the ligand upon binding of the ligand may 5 be determined using any of a range of conventional techniques.

The apparatus may comprise a single ligand which binds specifically to a single scaling ion, such that changes 10 in the electronic configuration of the ligand are directly related to the concentration of the scaling ion in the sample water.

More preferably, the apparatus may contain two or more 15 different ligands, for example three, four, or five or more. Alterations in the electronic configuration of each ligand may be determined independently, either simultaneously or sequentially.

20 In some embodiments, each ligand may bind specifically to a different scaling ion. Changes in the electronic configuration of each ligand are directly related to the concentration of the corresponding scaling ion in the sample water.

25 In other embodiments, each ligand may bind to two or more different scaling ions. Changes in the properties (i.e. the electronic configuration) of each ligand are directly related to the concentration in the sample water of the 30 two or more scaling ions to which that ligand binds.

Preferably, each ligand binds to a different combination of scaling ions such that the concentration of each individual scaling ion in the sample water may be

calculated from the measurements determined for two or more different ligands.

An advantage of the apparatus is that it allows *in situ* analysis to be performed, thereby avoiding the problems associated with transporting samples to the surface for *ex situ* analysis. The present invention is partly based on the realisation that electrochemical techniques can be adapted for performance downhole, i.e. in relatively demanding and hostile conditions.

Preferably the detector is operably connected to a processor for determining the concentration of scaling ions from the current or potential in the cell.

In some embodiments, the apparatus is adapted for use downhole (i.e. in a hydrocarbon well or aquifer).

The processor may also be adapted for use downhole, or alternatively it may be intended for remote installation e.g. at the surface. For example, the processor may be a suitably programmed computer.

A further aspect of the invention provides for the use of apparatus as described herein for *in situ* measurement of scaling ion concentration.

In another aspect the invention provides a method of monitoring the concentrations of scaling ions in downhole water comprising;

contacting a sample of downhole water with a ligand which selectively binds scaling ions, wherein the binding

of scaling ions in said sample to the ligand alters the electronic configuration of the ligand;

measuring changes in the electronic configuration of the ligand; and,

5 determining the concentration of said scaling ion from said changes in electronic configuration.

Brief Description of the Figures

Specific embodiments of the invention will now be described with reference to the following drawings, in 10 which:

Figure 1 shows an example of an apparatus according to one embodiment of the invention.

15 Figures 2 to 4 show examples of ligands suitable for use in accordance with an embodiment of the invention.

Figure 5 shows a flow diagram of a method of the present 20 claims.

Detailed Description of the Invention

In general terms, the present invention relates to the measurement of concentration of ions in downhole water, in particular ions responsible for scale formation by means of changes in the electronic configuration of a 25 ligand which binds scaling ions. A preferred approach involves the use of an electrochemical cell containing a ligand whose electroactivity changes on binding a scaling ion. Changes in ligand electroactivity upon ion binding alter the electrochemical properties of the cell and may 30 be measured using a detector. Other approaches may comprise the use of a ligand whose fluorescent properties change on binding of a scaling ion.

Downhole water may be comprised within a production fluid from a hydrocarbon well or reservoir, which may comprise hydrocarbons, drilling mud etc. The downhole water may,
5 for example, be connate water.

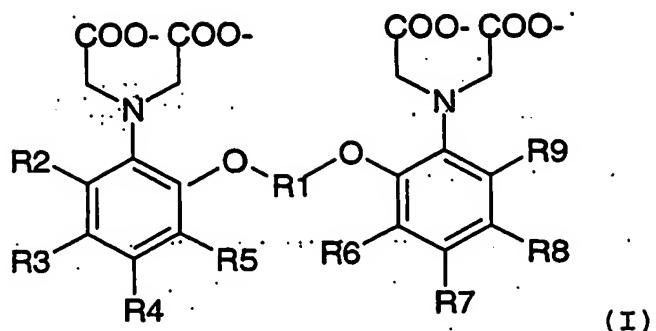
Scaling ions are ions which are responsible for the formation of scale. The principal scaling ions in downhole water are Ca^{2+} , Ba^{2+} and Sr^{2+} . A suitable ligand
10 may bind selectively to one or more of these scaling ions e.g. a ligand may bind to Ca^{2+} , Ba^{2+} and Sr^{2+} . Preferably, a ligand shows substantially no binding to other ions.

In some embodiments, the ligand may have a different
15 binding affinity for each of the three principal scaling ions (Ca^{2+} , Ba^{2+} and Sr^{2+}), allowing the levels of each individual ion in the downhole water to be determined. Discrimination between different ligands may be achieved, for example, by determining the characteristic redox
20 properties of each ligand at different potentials.

The ligand may be present in the cell in an aqueous solution at a concentration of 0.1 to 10mM, preferably 1 to 10mM, or may be dispersed within a porous polymer
25 membrane.

Ligands suitable for use in accordance with the invention are stable and able to bind scaling ions under downhole conditions, for example at high temperature (e.g. up to
30 175°C) and pressure (e.g. up to 1500 bar).

One class of suitable ligands have the formula (I):



where R1 is a C₁₋₅ alkyl (including, e.g. unsubstituted C₁-alkyl and substituted C₁₋₅ alkyl) or C₁₋₈ aryl

5 (including, e.g. unsubstituted C₁₋₈ aryl and substituted C₁₋₈ aryl); and,

10 R2 to R9 may independently be H, halogen (F, Cl, Br, I); C₁₋₅ alkyl group; O-C₁₋₅ alkyl group; COOH; NH₂; -CONH₂; CO-C₁₋₅ alkyl group; or a fluorophore group such as carboxy-X-rhodamine (ROX), tetramethylrhodamine (TAMRA) and fluorescein (FAM).

15 "C₁₋₅ alkyl" pertains to a monovalent moiety obtained by removing a hydrogen atom from a C₁₋₅ hydrocarbon compound having from 1 to 5 carbon atoms, which may be aliphatic or alicyclic, or a combination thereof, and which may be saturated, partially unsaturated, or fully unsaturated.

20 Examples of suitable ligands according to formula I are shown in Figure 2.

25 In some embodiments, the aromatic rings of suitable ligands may comprise substitutions in the ortho, meta or para positions (i.e. at one or more of positions R2 to R9), in order to shift the redox features of a ligand to allow scanning for the different ions in well-separated spectral windows, in order to prevent interference.

Other suitable ligands may include cryptands (Lehn & Sauvage (1975) J. Am. Chem. Soc. 97 23 6700), for example a ligand shown in Figure 3, and thymolphthalein and their derivatives (Qing and Yuying (1987) Talanta 34 6 555),
5 for example a ligand shown in Figure 4. Other suitable ligands may include neutral ionophores (Simon et al Anal. Chem. 1985, 57, 2756), specific crown ethers (D.J. Cram et al J. Am. Chem. Soc., 1973, 95, 3021) or antibiotics such as valinomycin (G. Eisenman et al, "progress in
10 surface and membrane science", J.F. Danielli et al ed., Vol. 6, Academic Press, New York, 1973, pp140-242)

The apparatus may further comprise a porous membrane which allows ions within the downhole water to pass into
15 the cell to contact the ligand. A suitable porous membrane may be made of zeolite or a ceramic material.

The membrane may be contacted with discrete samples or batches of downhole water or the membrane may be
20 contacted with a continuous flow of downhole water. The apparatus may comprise one or more liquid guidance channels to direct downhole water to the membrane and to remove downhole water after contact with the membrane.

25 The detector may comprise one or more electrodes which contact the ligand. Various arrangements of electrodes may be used as is conventional in electrochemistry.

Conveniently a three-electrode arrangement consisting of
30 a working electrode, a reference electrode and a counter electrode may be used. Preferably, the working electrode is composed of a material resistant to fouling, such as boron-doped diamond or glassy carbon, the counter

electrode is platinum and the reference electrode is Ag/AgCl. Other suitable electrode materials, such as AgI, are known to those skilled in the art.

- 5 The electrodes may be used to detect changes in the electroactivity of the one or more ligands. For example, electroactivity changes caused by the presence of scaling ions may alter the current flow or voltage between electrodes. Current or voltage may be detected or
- 10 measured by the detector. For example, the potential of the electrodes may be varied and the current measured or vice versa. The current or potential difference associated with the electroactivity of each of the one or more ligands may be measured by the detector and
- 15 correlated with the concentration of scaling ions in the downhole water sample. In the presence of the target ions, the peak current(s) should increase, proportional to the concentration of the target species. A power source may be connected to the electrodes to drive the
- 20 current between the electrodes. The power source may be an integral part of the apparatus, and, for example, may be comprised within the detector. In other embodiments, the power source may be separate from the apparatus and connectable thereto. The apparatus may comprise
- 25 appropriate circuitry for connection to the power source.

The ligand may be contained within the apparatus in any of a number of ways. In some embodiments, the ligand may be dispersed in an aqueous solution within a chamber of the apparatus. In other embodiments, the ligand may be dispersed within a porous polymer membrane. Binding of the scaling ions by the ligand occurs within the pores of the membrane and resultant changes in current or

potential are detected by circuitry connected directly to the membrane via the working, counter and reference electrodes. The use of a porous membrane is convenient in allowing the miniaturisation of the voltammetric or 5 amperometric sensor, thus leading to faster response times, lower consumption of reagents and lower unit costs.

In other embodiments, the ligands may be attached to 10 conducting solid particles, such as carbon or a metal (e.g., gold), which are incorporated into the surface of one or more of the electrodes, preferably, the working electrode. The accumulation of particles with attached ligand forms a conducting porous electrode with ligand 15 attached to the walls of the pores. Suitable techniques for fixing the particles to the electrode surface include epoxy resin adhesion or abrasive immobilisation. A porous electrode for hydrogen sulfide determination, for example, is described in co-pending application 20 GB0217249.2.

For example, the ligand (I) above may be designed such that group R8 is an amine ($-\text{NH}_2$), which can be reacted with nitrous acid to form the diazonium ion $-\text{N}^+ \equiv \text{N}$ and 25 subsequently coupled to carbon particles by reduction of the diazonium group by hypophosphorous acid. The ligand is thus chemically bonded to the carbon particles and these can be incorporated into the working electrode 4 as described above. In other embodiments, the ligand (I) 30 above may be coupled to gold particles with one of the groups R2 to R9 being either an amine ($-\text{NH}_2$) or a thiol ($-\text{SH}$).

As described above, the detector may be operably connected to a processor that determines the concentration of scaling ions in the sample from the current or potential difference measured by the detector.

5 The processor may be separate from or part of the detector. The processor may also be adapted for use under downhole conditions (i.e. high temperature, high pressure and high salinity). Alternatively, it may be intended for remote installation e.g. at the surface. For example,

10 the processor may be a suitably programmed computer.

The measurement of scaling ion concentrations as described herein may be useful in downhole sampling, production logging to characterise flow into the well, and thereby aid remediation or production strategies, and 15 in permanent monitoring applications, where the build up of scale or water breakthrough/flooding of the reservoir might be gauged.

20 Figure 1 shows a diagram of an apparatus according to one embodiment of the invention. Inlets and outlets for sampling downhole water are as indicated. The sample water contacts a membrane 1 which allows the passage of ions into the cell 5. The ligand solution in the cell 5 is contacted by a Ag/AgCl reference electrode 2, a 25 platinum ring counter electrode 3 and a glassy carbon working electrode 4. The electrodes 2, 3, 4 detect changes in the electroactivity of ligand in the cell 5 which are related to scaling ion concentration.

30

In an example according to an embodiment of the invention, the four ligands (1-4) shown in Figure 2 may be present in solution in cell 5.

These ligands have different binding properties; ligand 1 binds Ca^{2+} , Sr^{2+} and Ba^{2+} ; ligand 2 binds Ca^{2+} and Sr^{2+} , ligand 3 binds Sr^{2+} and Ba^{2+} and ligand 4 binds Ba^{2+} .

5

The level of Sr^{2+} in the sample water may be determined, for example, by measuring the alterations of the electroactivities of ligands 3 and 4 in the cell and then subtracting the value obtained for ligand 4 from value 10 obtained for ligand 3, to provide a value which represents the concentration of Sr^{2+} . (i.e. 3 - 4 = $[\text{Sr}^{2+}]$).

The level of Ca^{2+} in the sample water may be determined by 15 measuring the alterations of the electroactivities of ligands 2, 3 and 4 in the cell. The values for ligands 2 and 4 are added together and the value obtained for ligand 3 is subtracted from this combined figure, to provide a value which represents the concentration of 20 Ca^{2+} . (i.e. 2 + 4 - 3 = $[\text{Ca}^{2+}]$).

The level of Ba^{2+} in the sample water is determined by measuring the alterations of the electroactivities of ligands 1 and 2 in the cell and then subtracting the 25 value obtained for ligand 2 from the value obtained for ligand 1, to provide a value which represents the concentration of Ba^{2+} . (i.e. 1 - 2 = $[\text{Ba}^{2+}]$ or ligand 4).

While the invention has been described in conjunction 30 with the exemplary embodiments described above, many equivalent modifications and variations will be apparent to those skilled in the art when given this disclosure. Accordingly, the exemplary embodiments of the invention

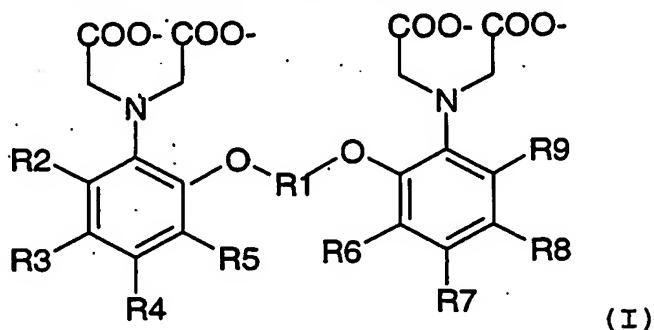
set forth above are considered to be illustrative and not limiting. Various changes to the described embodiments may be made without departing from the spirit and scope of the invention.

Claims:

1. An apparatus for determining the concentration of scaling ions in downhole water; the apparatus comprising;
 - 5 a ligand which binds scaling ions in a sample of downhole water, said ligand having an electronic configuration which is altered on binding of a scaling ion, and;
 - 10 a detector for determining alterations in said electronic configuration, the amount of said alterations being indicative of the concentration of the scaling ion in the sample.
2. An apparatus according to claim 1 wherein the scaling ion is selected from the group consisting of Ca^{2+} ,
15 Ba^{2+} and Sr^{2+} ions.
3. An apparatus according to claim 1 or claim 2 wherein the detector comprises one or more electrodes for
20 determining changes in the electroactivity of said ligand.
4. An apparatus according to claim 3 wherein the ligand is immobilised on conducting particles attached to one or
25 more of said electrodes.
5. An apparatus according to claim 4 such that wherein said conducting particles are carbon or metal particles.
- 30 6. An apparatus according to claim 5 wherein the metal particles are gold particles.

7. An apparatus according to any one of claims 4 to 6 wherein said particles with immobilised ligands thereon form a conducting porous electrode.

5 8. An apparatus according to any one of the preceding claims wherein the ligand has the formula:



where R1 is a C₁₋₅ alkyl (including, e.g. unsubstituted 10 C₁₋₅alkyl and substituted C₁₋₅ alkyl) or C₁₋₈ aryl (including, e.g. unsubstituted C₁₋₈ aryl and substituted C₁₋₈ aryl) and;

R2 to R9 are, independently, H, halogen (F, Cl, Br, I); C₁₋₅ alkyl group; O-C₁₋₅ alkyl group; COOH; NH₂; -CONH₂; 15 CO-C₁₋₅ alkyl group; or a fluorophore group.

9. An apparatus according to claim 8 wherein the ligand is a ligand shown in Figure 2.

20 10. An apparatus according to any one of the preceding claims comprising a processor for calculating the concentration of the scaling ion in the sample water from alterations in the electronic configuration of the ligand

25 11. An apparatus according to claim 10 comprising two or more different ligands, said detector being adapted to determine alterations in the electronic configuration of each ligand independently.

12. An apparatus according to claim 11 wherein each of the said two or more ligands binds to a different combination of scaling ions.

5

13. An apparatus according to claim 12 comprising two or more of the ligands shown in figure 2.

14. An apparatus according to any one of claims 11 to 13
10 wherein the processor is adapted to calculate the concentration of each individual scaling ion in the sample water from the alterations in electronic configuration determined for each of the two or more different ligands.

15

15. An apparatus according to any one of the preceding claims comprising a porous membrane which allows ions from the downhole water to contact the ligand.

20 16. An apparatus according to claim 15 wherein the membrane is ceramic or zeolite.

17. An apparatus according to any one of the preceding claims which is adapted for downhole operation.

25

18. A method of monitoring the concentrations of scaling ions in downhole water comprising;

30 contacting a sample of downhole water with a ligand which selectively binds scaling ions, wherein the binding of scaling ions in said sample to the ligand alters the electronic configuration of the ligand;

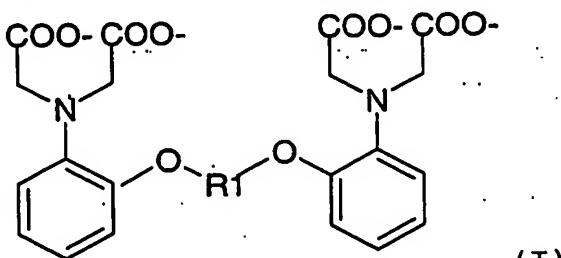
measuring changes in the electronic configuration of the ligand; and,

determining the concentration of said scaling ion from said change in electronic configuration.

19. A method according to claim 18 wherein the scaling ions are selected from the group consisting of Ca^{2+} , Ba^{2+} and Sr^{2+} ions.

20. A method according to claim 18 or claim 19 wherein the change in electronic configuration is determined by measuring alterations in the electroactivity of the ligand.

21. A method according to any one of claims 18 to 20 wherein the ligand has the formula:



15

where R1 is a C_{1-5} alkyl (including, e.g. unsubstituted C_{1-5} alkyl and substituted C_{1-5} alkyl) or C_{1-8} aryl (including, e.g. unsubstituted C_{1-8} aryl and substituted C_{1-8} aryl); and,

R2 to R9 may independently be H , halogen (F , Cl , Br , I); C_{1-5} alkyl group; O-C_{1-5} alkyl group; COOH ; NH_2 ; CONH_2 ; CO-C_{1-5} alkyl group; or a fluorophore group.

22. A method according to claim 21 wherein the ligand is a ligand shown in Figure 2.

23. A method according to any one of claims 18 to 22 comprising contacting the sample with two or more

different ligands and determining alterations in the electronic configuration of each ligand.

24. A method according to claim 23 wherein each of the 5 said two or more ligands binds to a different combination of scaling ions.

25. A method according to claim 23 or claim 24 comprising calculating the concentration of each scaling 10 ion in the sample water from the alterations in electronic configuration determined for each of the two or more different ligands.

26. Use of an apparatus according to any one of claims 1 15 to 17 in a method of determining the concentration of a scaling ion in downhole water.

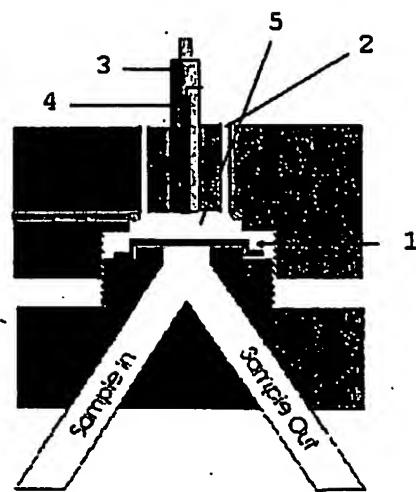
27. Use of a ligand as shown in any one of Figures 2 to 4 in a method of determining scaling ion concentrations 20 in downhole water.

28. An apparatus or method for determining scaling ion concentrations in downhole water which is substantially as herein described with reference to the accompanying 25 drawings.

ABSTRACTAPPARATUS AND METHOD FOR MEASURING CONCENTRATIONS OF IONS5 IN DOWNHOLE WATER

This invention relates to methods and apparatus for determination of ion concentrations in downhole water from hydrocarbon wells, aquifers etc. This is useful in a 10 wide range of applications, including predicting the formation of scale and fingerprinting waters from different sources. More particularly, the invention relates to the use of ligands whose electronic configuration is altered by the binding of the scaling 15 ions within a water sample. These alterations are detected, for example by electrochemical means, and are indicative of the concentration of scaling ions in the sample.

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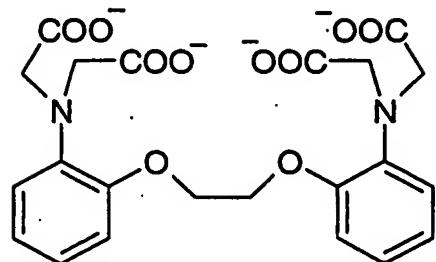
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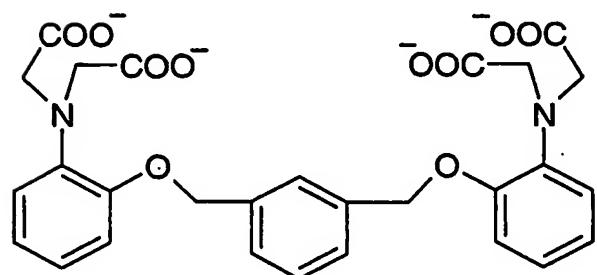
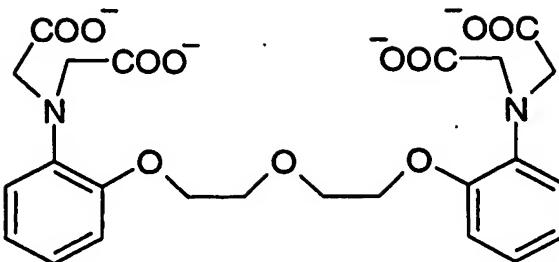
Figure 1

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Ligand 1

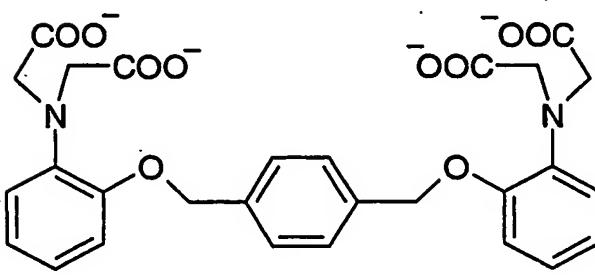


Ligand 2



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Ligand 3



Ligand 4

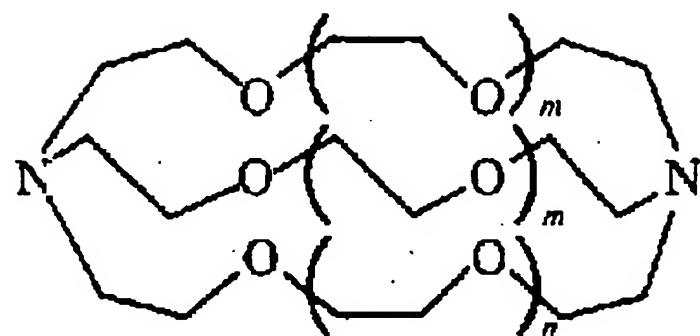
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Figure 2

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5



- 1, $m = 0; n = 1$ [2.1.1]
- 2, $m = 1; n = 0$ [2.2.1]
- 3, $m = n = 1$ [2.2.2]
- 4, $m = 1; n = 2$ [3.2.2]
- 5, $m = 2; n = 1$ [3.3.2]
- 6, $m = n = 2$ [3.3.3]

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Figure 3

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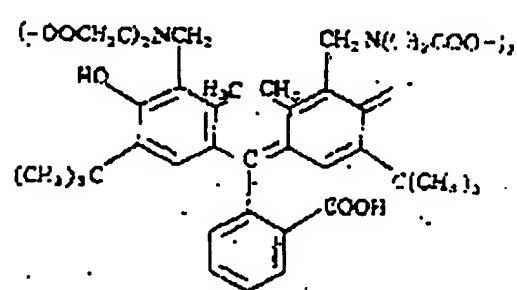
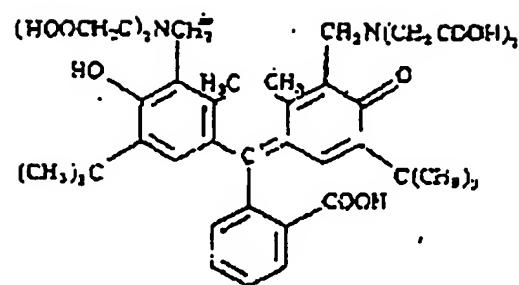


Figure 4

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Contact a sample of downhole water with a ligand
which selectively binds scaling ions



Measure changes in the electronic configuration
of the ligand



Determine the concentration of said scaling ion
from said change in electronic configuration

Figure 5

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